Water Activity in Viscous Heterogeneous Bio-systems

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Classical Thermodynamics does not treat the effects of the medium viscosity as long as it deals with equilibrium states. Unfortunately, this has consequences on the experimental practices and on the reliable characterization of the immense variety of bio-systems and bio-products that are rather viscous and heterogeneous. Since most of them are aqueous or contain aqueous phases, one is inclined to use water as an internal probe to describe their behavior and water activity, a_W, as a suitable parameter.

When the viscosity of a condensed phase is large, as in many real systems, the migration of water can be very slow. This is why any steady state can mimic the attainment of equilibrium and the detected water activity may have a value, $a_{W,app}$, smaller than the true one.

An alternative approach is therefore necessary to reconcile expectations from a thermodynamic description of an aqueous (or simply moist) system with the experimental difficulties related to the low mobilityof the water molecules, u_W.

Some NMR experimental evidence was provided by Brian Hills who proposed a correlation between a_W and the normalized overall FID relaxation rate, which can be related to u_W. At least at the microscopic level, namely, the level "seen" with a NMR investigation, u_W and a_W would accordingly be someway correlated to each other, in spite of the fact that u_W and a_W belong to different realms of physics.

In present work advantage is taken from the fact that every viscous aqueous system can be imagined as obtained from a starting poorly viscous solution either by isothermal dehydration, or by cooling (or combination of these treatments), so to approach the glass transition threshold, across which viscosity and heat capacity undergo large changes.

The formal treatment of the problems starts with an expression of the chemical potential of water that includes an extra contribution to the overall potential energy of the aqueous phase(s), namely, a fraction of the “free energy” that becomes available once the viscosity drops down.

$$\mu_W = \mu_W^* + RTlna_W - \mu_{visc} = \mu_W^* + RTlna_{W,app}$$

The explicit form of the μ_{visc} comes from the one proposed by Gibbs and Di Marzio to describe the connection between the excess (with respect to the solid state) configuration part of the Helmholtz free energy F_c^{exc} to the viscosity, η, of a liquid close to its glass transition threshold, namely,

$$\ln\eta = \beta - \alpha F_c^{exc}/RT$$

$$\frac{\mu_W^{visc}}{RT} = -ln\frac{a_W}{a_{W,app}} = \alpha\frac{F_c^{exc}}{RT} = \beta - \ln\eta$$

When η approaches the viscosity of pure water, η^*, $a_{W,app}$ approaches a_W, that approaches unity: thence $\beta = ln\ \eta^*$. This allows the conclusion that, at any temperature,

$$\frac{a_W}{a_{W,app}} = \left(\frac{\eta}{\eta^*}\right) = \left(\frac{u_W^*}{u_W}\right) \geq 1$$

where the mobility has been replaced with the reverse of the viscosity, η, experienced by water molecules that migrate from the core to the surface of the system. Similar expressions are proposed to describe the effects of physical barriers that hinders water displacements across heterogeneous systems.